Transfer leak studies and comparisons of primary leak standards at the National Bureau of Standards and Sandia National Laboratories

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Primary leak standards are being developed at the National Bureau of Standards (NBS), and a cooperative NBS–Sandia National Laboratories (SNL) program is underway to compare their different primary standards and investigate the properties of transfer leaks. Initial results of comparisons of the primary standards at the two laboratories, accomplished via sintered metal transfer leaks in the range 5×10^{-12} to 5×10^{-9} mol/s, show that the calibration methods used in the two laboratories agree to within a few percent for nitrogen, argon, and helium. Significant instabilities with time have been observed for one of the two leaks used in the comparison. Temperature coefficient data for helium diffusion leaks are presented which illustrate the possibility of significant errors when a linear temperature dependence is assumed over too wide a temperature range.

I. INTRODUCTION

The need for improved leak measurement accuracy in a variety of industries, and in some cases for legal traceability to a recognized standards authority, has prompted the development of leak standards at the National Bureau of Standards (NBS). The Sandia National Laboratory (SNL) Primary Standards Laboratory has had a long standing leak standards and calibration program. A common interest in the properties of transfer ("standard") leaks and the opportunity to compare primary standards utilizing different physical principles has encouraged a cooperative research program between the two laboratories. This paper discusses the NBS and SNL primary standards, automated helium leak comparators in use at both laboratories, and the results of an NBS–SNL leak standard comparison which also yielded data on transfer leak stabilities. Temperature effects on leak rates of encapsulated helium diffusion leaks are also discussed.

II. DESCRIPTION OF APPARATUS AND METHODS FOR ABSOLUTE CALIBRATION

A. NBS

The primary leak apparatus that has been developed at NBS is shown schematically in Fig. 1. This apparatus benefits from considerable development work done in the NBS high vacuum standards program. The standard is divided into three major components: the vacuum chamber, the leak manifold, and the flowmeter. The flowmeter will be described in detail in Ref. 1, and the vacuum chamber is similar to that described in Ref. 2.

To calibrate a leak on the NBS system, the leak is placed on the manifold, and the entire system is evacuated. The flowmeter is isolated from the rest of the system, and gas from the unknown leak is allowed to flow into the vacuum chamber, through an orifice, and is then evacuated by the pump. After the gas flow and upper chamber pressure reach equilibrium, the upper chamber pressure indication is re-corded. The leak stand is then valved off from the vacuum chamber, the flowmeter is pressurized with the gas species of interest, and the flow is adjusted so that, when everything has stabilized, the upper chamber pressure indication is the same as when flow from the leak was passing through the system. The flow rate is now measured by valving off the variable volume from the reference volume and activating a capacitance diaphragm gauge (CDG) driven servo mechanism that drives the piston into the variable volume at a rate that will keep the pressure in that volume constant as gas flows into the vacuum chamber. By measuring the rate at which the piston is advanced, and knowing the cross sectional area of the piston and the temperature and pressure of the gas in the variable volume, the flow rate into the main chamber can be calculated. To within limits determined by the instabilities of the upper chamber pressure gauge, this measured flow rate can then be equated to the flow rate of the unknown leak, and the calibration is complete.

The limits of this technique are at present largely determined by the capabilities of the flowmeter. Evaluation of the flowmeter is still under way, but at this time it appears that the measurements can be made with random errors on the order of 5% at 5×10^{-11} mol/s, less than 1% near 2×10^{-10} mol/s, and about 0.5% near 5×10^{-8} mol/s.[6] To this must be added an estimated systematic uncertainty of 1% or less.

B. SNL

Reference 3 describes the various methods used by SNL for the calibration of leak artifacts. The method of particular interest here is the "$P \Delta V$" method, as it was used to calibrate the artifacts transferred between NBS and SNL to date.

In this method, the flow from the leak is allowed to pressurize a volume to some predetermined pressure, P. A known volume ΔV is then added to the system and a timer started. When the pressure returns to the value at which the

FLOWMETER   CHAMBER   LEAK MANIFOLD
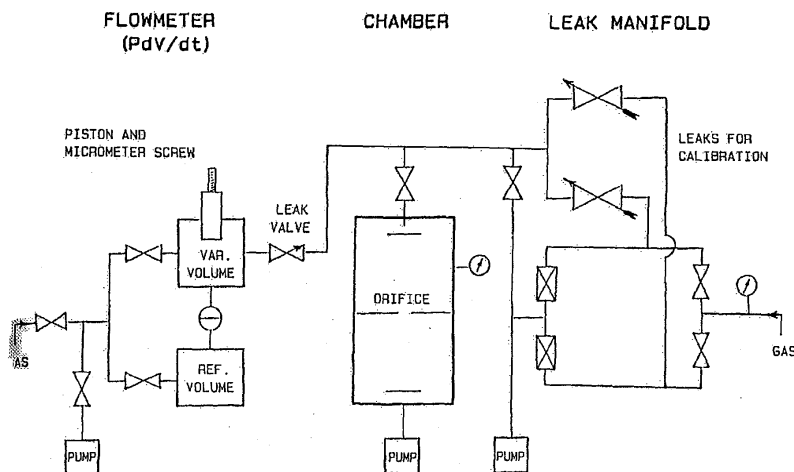(PdV/dt)

FIG. 1. Schematic diagram of the NBS primary leak standard, showing the flowmeter, vacuum chamber, and manifold on which leak artifacts to be calibrated are mounted.

known volume was added, the timer is stopped, with Δt seconds having elapsed. By dividing the quantity $P \, \Delta V / \Delta t$ by the product of the gas constant and the absolute temperature of the leak, the flow rate can be calculated. The overall uncertainty for the SNL primary standard is $\pm 3\%$ for flow rates in the range 10^{-7} to 10^{-11} mol/s.

III. NBS/SNL COMPARISONS

Two sintered metal leak artifacts were calibrated at SNL, then at NBS, and again at SNL. This comparison was made to expose possible systematic differences between the standards of the two laboratories, and also to begin the assessment of the long-term stability of the artifacts themselves.

The leaks, designated as 49 and 152, have leak rates which are roughly proportional to the supply pressure, although for the same supply pressure the flow rates of 152 are about a factor of 200 less than those of 49. Calibrations were done in both laboratories with He, N_2, and Ar. SNL performed the first set of calibrations in February 1984. NBS then performed a second set in September–October 1984, and a third in December 1984–January 1985. SNL has completed a fourth set during the summer of 1985. As noted below, leak 152 exhibited large shifts so its use was discontinued after the second NBS calibrations.

The leak conductances at 23 °C were calculated by multiplying the measured flow rate in mol/s by RT, where R and T are, respectively, the gas constant and absolute temperature in Kelvin ($T = 296.15$ K), then dividing by the pressure applied to the upstream side of the leak. For each gas, the conductances from all calibrations were least-squares fitted to a single linear function of the applied pressure. The residuals, i.e., differences between the experimental data and the fitted curves, expressed in percent, are shown for leak 49 in Fig. 2 for nitrogen. (There was no second NBS calibration for No. 49 with nitrogen.) The residual plots for the other two gases are similar and, in fact, those points all lie within the range of Fig. 2.

The results are affected by an apparent small drift in the leak as indicated in Fig. 2 by the systematic changes between the sequential data sets. Similar changes are found in the argon and helium data. However, the results can still be used to estimate the upper bounds on the possible differences between the two laboratories. Data were obtained by both laboratories at flow rates ranging from 1.1×10^{-10} to 9.2×10^{-8} mol/s for He, from 2.0×10^{-10} to 6.0×10^{-8} mol/s for N_2, and from 1.7×10^{-10} to 4.8×10^{-8} mol/s for Ar. Examples of maximum differences between data and the fitted curves, accounting for all three gases, were 0.8% at a flow rate of 6.0×10^{-8} mol/s, 2.4% at 2.6×10^{-8} mol/s, 2.4% at 2.3×10^{-10} mol/s, and 3.4% at 2.1×10^{-10} mol/s. Since these differences include the apparent drift of the leak with time mentioned above, 3% is considered to be a conservative estimate to the upper bounds of the systematic differences between the calibration methods of NBS and SNL for flow rates from about 1×10^{-10} to 9×10^{-8} mol/s. The 3% limit is indicated by the dotted lines in Fig. 2.
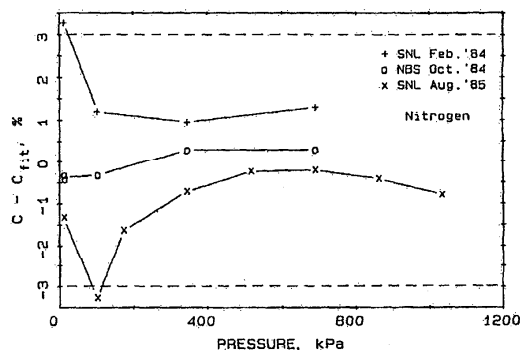

FIG. 2. Percentage differences, for sintered metal leak 49, between experimental conductances and the curve generated from a least-squares fit of the nitrogen conductances vs applied pressure. All conductances determined at NBS and SNL over period of 2 years were used in the fit.

For the low-range leak 152, differences between the two NBS calibration sets for each gas were on the order of 15%–20%. These results were obtained at the same time the reproducible results were obtained on 49, indicating that the variations were most likely in 152 itself. Over periods of a few days 152 was stable enough to permit an analysis of short-term errors in the NBS flowmeter. Short-term instabilities on the order of 25% were found at flow rates on the order of 7×10^{-12} mol/s, and helped establish an upper bound for the random errors of the NBS flowmeter in that range.

The quite different levels of long-term instability for the two leaks are consistent with the experiences in the Sandia primary standards laboratory with other sintered metal leaks in this general flow range. For sintered metal leaks in the 10×10^{-8} to 10^{-11} mol/s flow range, German[4] has documented changes on the order of 10% when in unfavorable environments. His work shows shifts towards both larger and smaller flow rates. It should be noted that SNL experience also indicates that in general the stability of sintered metal leaks improves as the leak magnitudes increase.

IV. DESCRIPTION OF APPARATUS AND METHOD FOR COMPARATIVE CALIBRATIONS OF He DIFFUSION LEAKS

Helium permeation leaks are widely used for leak detector calibration, and a whole technology is devoted to these artifacts. Reference 3 describes a comparison method for calibrating this type of leak which covers the range from 1×10^{-8} to 1×10^{-14} mol/s. It uses a commercial helium leak detector as its major component, and permits the output from a calibrated leak to be valved through the mass spectrometer of the leak detector to obtain a reading, after which the output from the unknown leak is valved through the leak detector and another reading taken. To within the linearity and stability of the helium leak detector, the ratio of the two readings on the detector is the ratio of the helium leak rates.

Several precautions must be observed when using He permeation leaks. The artifacts have a large temperature coefficient, on the order of 2%–5% of the value °C. This means that the temperature of both the standard and unknown must be carefully monitored during the calibration. Also, since leaks may be used over a wide temperature range, calibrations must be made over a corresponding range. To this end, the comparators have been equipped with an air bath within which the unknown leak can be temperature controlled from − 15 to 60 °C to within ± 50 mK.

The curve in Fig. 3 shows the results of a typical comparison between two helium diffusion leaks, where the one designated as the "unknown" has been cycled through a temperature range from − 14 to + 60 °C. The unknown leak had been assigned a value by the supplier at 26.11 °C and was reported to have a constant temperature coefficient of 3.5%/°F. Figure 3 compares this "calibration" with the values measured on the comparator. The data have been normalized to agree at 26.11 °C. Also shown are results from a "calibration" using a constant temperature coefficient of 3.5%/°C. Clearly the Fahrenheit value is incorrect and the value
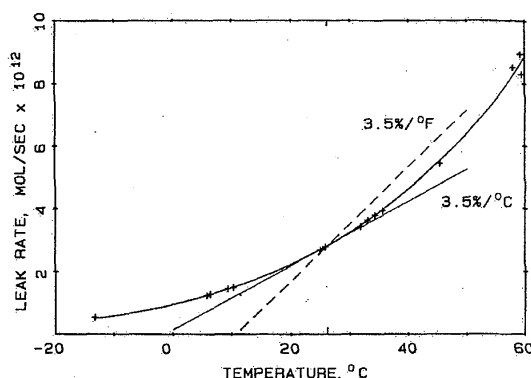

FIG. 3. Typical He permeation leak rate curve as a function of temperature. Curve results from a least-squares fit to data (+) using Eq. (2). Straight lines show predicted leak rates based on constant temperature coefficients of 3.5%/°C and 3.5%/°F when the calibration was performed at 26.11 °C.

should have been reported in degrees Celsius. SNL has found this mistake repeated with several other leaks. Beyond this gross error, Fig. 3 shows that even if a "proper" value (i.e., 3.5%/°C) of a constant temperature coefficient is assumed, large errors can result from its use. At 40 °C the error relative to the fitted curve is 10% and at 10 °C it is 18%. The discrepancy between the measured leak rates and those obtained from a linear extrapolation can be minimized by the use of a more realistic temperature function. For example, if the permeation rate equations given by Dushman[5] are used, along with the ideal gas law for the temperature dependence of the pressure within the closed reservoir found on most helium permeation leaks, the overall temperature dependence of the leak rate L can be shown to be

$$L = A \times T \times e^{-B/T}, \qquad (2)$$

where T is the Kelvin temperature. The constant A, which is proportional to the permeability, and B, which is the activation energy divided by the gas constant, are to be determined by a least-squares fit. For the data of Fig. 3, the constants A and B are, respectively, 2.558×10^{10} and 3049 K if L is in mol/s. Fitted results for five other leaks whose flow rates near 25 °C were between 9×10^{-13} and 6×10^{-11} mol/s gave values for B which were not correlated with leak rate, and ranged from 2932 to 3050 K. The six leaks were from three different manufacturers, and the differences in the B values probably reflect differences in the composition of the glass diffusion elements. The A values are of no particular interest because none of the leak rates were determined by comparison with calibrated standards.

The standard deviations of the leak rates predicted from the six fits give an indication of the random uncertainties associated with the comparison method used. For the six leaks studied, three standard deviations of the predicted leak rates are on the order of 0.6% of the values at 0 and 50 °C and on the order of 0.3% of the values at 25 °C.

The leak comparator uses a tuned mass spectrometer as its detector, and such devices can exhibit nonlinearities. The mode of operation of the NBS/SNL helium leak compara-

tors tends to alleviate any such linearity problem, since leaks of comparable values are generally compared.

Another important factor in the use of permeation leaks is equilibration times. In cases where the artifact has been stored with its outlet valve closed, the concentration gradient of interstitial helium in the permeation element will be altered. Depending on how long the valve has been closed, and the temperature of the element, the excess helium may cause significant errors for some time after the leak is re-evacuated. Experience shows that in general the flux from the artifact decays exponentially with time, asymptotically approaching equilibrium. For an artifact with a leak rate of 2.4×10^{-12} mol/s which had been stored with the outlet valve closed for two weeks, the flow rate at 25 °C was 30% higher than its equilibrium value after 2 h, and about 12 h were required for the rate to return to within 2% of its equilibrium value. Data also show that at 23 °C significant equilibration times are associated with leaks which have not had the valve closed. An hour or more is required after the leak is evacuated for the leak rate to approach within a few percent of its equilibrium value.

Equilibrium times are dependent on the temperature and the design of the artifact in use, as well as on its past history. Significant periods may also be required for a leak detector vacuum system to equilibrate after a shutdown or when it has been exposed to gross amounts of helium. Therefore, it seems prudent to allow for at least an overnight (about 16 h) equilibration time before attempting accurate leak measurements.

V. SUMMARY

Data have been presented which indicate that the upper bound on systematic differences between the two very differ-ent types of primary standards for the calibration of leak artifacts in use at NBS and SNL is about 3% for flow rates on the order of 1×10^{-10} to 9×10^{-8} mol/s. The two sintered metal leaks used in the comparison process behaved quite differently. One changed by less than 4% over an 18-month period, the other by more than 15% in 3 months. Large errors can arise from the assumption of a linear temperature coefficient when using helium permeation leaks. Had the leak of Fig. 3 been calibrated at 38 °C and used at 25 °C, the error at the latter temperature would be about 45% relative to the fitted curve.

When a permeation leak is placed into a system, it should be allowed to equilibrate at least overnight before use. This is absolutely necessary if the leak has been stored with its outlet valve closed.

ACKNOWLEDGMENTS

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[6]1 mol/s = 2.2135×10^4 cm³/s at 0 °C and 101325 Pa.